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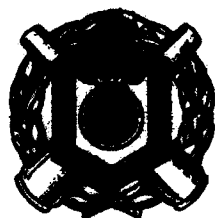
**REACTION KINETICS OF HAN AND WATER MIXTURES USING A
PERSONAL COMPUTER**

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ARDEC

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<p>A program has been developed to study the reaction kinetics of gun propellants such as the HAN based liquids using a personal computer. These HAN based systems can be studied using a main-frame computer but often require long run times. In order to eventually model the liquid propellant guns, including the fluid flow, it was necessary to develop a fast reacting program which would form part of the final system. In addition, a reaction program which could run on a personal computer is convenient for initial testing of possible fuels and oxidizers. The main problem with any such system is that the equations are stiff with ideal time steps varying from 10E-18 seconds to 10E+03 seconds. Under these conditions, many integration schemes become unstable. An additional problem of using a PC is that the accuracy is limited, and as a result, atoms are not conserved due to round-off error. A minimum free energy chemical equilibrium code MCVEC was used to calculate equilibrium conditions. Using these equilibrium conditions, the reaction kinetic code was used to study the reaction of hydrogen and oxygen as an initial test case. Comparisons were then undertaken using HAN and the results compared with both the equilibrium results and available experimental data.</p>					
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INTRODUCTION

Propellant formulators and ballisticians have been using thermodynamic codes such as Blake, Nasa-Lewis, and more recently MCVEC (refs 1 through 3, respectively) to predict various thermodynamic parameters and combustion products for gun firings. The critical assumption used in applying these codes is that sufficient time has elapsed during the interior ballistic cycle to achieve a state of minimum free energy (chemical equilibrium) within the combustion chamber. The validity of this assumption, however, has not been determined, and as a result, should be thoroughly investigated. In theory, this could be done by analyzing the chamber combustion products and comparing them with the equilibrium code data.

Since experimental gun-shot data are not always available, theoretical methods involving chemical kinetics can be employed to map the reaction paths and predict the species generated during the interior ballistic cycle. The magnitude of this undertaking, however, requires the use of computers to perform the calculations efficiently. Several codes which model chemical kinetics are available for this purpose, but unfortunately these existing computer codes are written for either main-frame computer application or require long run times.

Recent developments in using virtual memory on personal computers have guided the initial intention of this effort to develop a kinetic code which will run on a desk-top computer and yet not require extensive running time. Using such a system, it may be possible to perform an approximate gun calculation on a personal computer. The ultimate goal, however, is to model the propellant combustion including both the reaction kinetics and propellant hydrodynamics. Therefore, a chemical reaction kinetics code was written for use on a personal computer which would eventually form part of the larger program. In addition, such a code would be useful as a tool to supplement the chemical equilibrium codes currently in use.

To test the validity of the assumptions incorporated into the algorithm of the code, the oxidation of hydrogen at various conditions was run and compared against the results from the equilibrium code. It is difficult to undertake a comparison with steady state experimental results as most experiments have been performed at between 1000 K and 2000 K where the main product is water.

The initial propellant selected to develop this kinetic code was the HAN based liquid propellant system (LP1845 and LP1846). This selection was based on the current interest in HAN based regenerative liquid propellant guns and the apparently simple molecules involved in LP formulations: HAN (NH_3OHNO_3), TEAN ($\text{C}_2\text{H}_5\text{O}$)₃ NHNO_3 , and water (H_2O).

Only the oxidation of anhydrous HAN is discussed in this report. The kinetic code results are compared to equilibrium code data as a first approximation goodness-of-fit. However, since the test of any modeling scheme should be agreement with experimental data, the kinetic code results are also compared with experimental thermal decomposition data.

METHOD OF CALCULATION

The equations required for the chemical kinetics of the fluid system will involve variable temperature and density. The present calculations were undertaken at constant density as this is most easily compared with the minimum free energy calculations. The changes required to allow variable density are minimal. The basic equation for the change of the concentration c of the i th species is

$$\frac{dc_i}{dt} = \sum \beta_{ij} r_j \quad (1)$$

where β_{ij} is the i th species in the j th equation and r_j is defined as the net rate by the mass-action equation

$$r_j = k_f \prod c_i - k_r \prod c_i \quad (2)$$

where the forward reaction of rate k_f is related to the reverse reaction rate k_r by the equilibrium constant K_{eq}

$$\frac{k_f}{k_r} = K_{eq} \quad (3)$$

The equilibrium constant used expresses the ratio between the number of moles of products and the number of moles of reactants. In the case where the number of moles of products and reactants are the same, then $K_{eq} = K_p$ the usual equilibrium constant. In the case that

$$\Delta N = \sum N_p - \sum N_r \quad (4)$$

is not zero, then

$$K_{eq} = K_p (RT)^{-\Delta N} \quad (5)$$

In the case studied here, the pressure P will rise according to the relation for ideal gases

$$\frac{dP}{dt} = RT \sum \frac{dc_i}{dt} \quad (6)$$

Equation 1 is used to integrate the change in concentration in time. Conceptually, the integration of this derivative is quite straightforward, but the real difficulties are imposed by the limitation in accuracy of the computer. The first problem is the fact that the integration scheme may become unstable with time steps which are too large. This can be overcome by various methods. The most common method involves calculating the high order derivatives (for example, the first four derivatives and enforcing continuity in all derivatives). A major problem with this method is that sudden changes cannot be made in a variable. These changes must be undertaken gradually. This is satisfactory on a main-frame computer where calculation time is not the chief concern. When solving the problem on a PC with reasonable run time, it is necessary to be able to make approximations which require sudden changes in the function in order to conserve certain quantities (e.g., atom numbers). Therefore, a semi-implicit time advanced scheme (ref 4) was chosen.

If equation is written as

$$\frac{dx_i}{dt} = P_i - x_i L_i \quad (7)$$

where P_i are the production terms and L_i are the loss terms for the species x_i . The usual finite difference form of the semi-implicit scheme is

$$\frac{x_i(j+1) - x_i(j)}{t} = P_i(j) - x_i(j+1)L_i(j) \quad (8)$$

where the right hand side can be written as $\left[\frac{1}{1 + tL_i(j)} \right] f(j)$. Now equation 7 can be approximated by

$$\frac{dx_i}{dt} = P_i(t_j) - x_i(t)L_i(t_j) \quad (9)$$

integrating equation 9 we obtain

$$\frac{x_i(j+1) - x_i(j)}{t} = \left[\frac{1 - e^{-tL_i(j)}}{tL_i(j)} \right] f(j) \quad (10)$$

where t is the time step. This scheme is very stable and the original paper should be consulted for details.

The second problem involves dealing with a large range in the time derivatives. In this case, the range is quite large because the reaction rates vary from $10\text{E}-18$ to $10\text{E}+20 \text{ sec}^{-1}$. These equations are known as stiff, and various schemes have been proposed to handle them. For example, if the computer can retain 12 significant figures and the time step is chosen as $10\text{E}-8 \text{ sec}$, then only the last couple of digits of the smallest derivative will be involved while the largest derivative will not be involved. The number of time steps to perform an integration will be prodigious for a PC.

The critical mechanism for propellant combustion is to decompose the initial ingredients into reactive gaseous species that will drive the reactions. This is the overall rate-determining step and the sequence of subsequent time steps must be chosen around this rate. This is necessary in order to make the propellant decompose to start the reaction.

As a first approximation, the initial shortest time step for the reaction ($10\text{E}-18 \text{ sec}$) is arbitrarily set to equal one tenth the value of the fastest reaction characteristic time (in this case $10\text{E}-17 \text{ sec}$). A characteristic time for a given reaction is defined as the maximum time required to use up one of the reactants and is approximately the reciprocal of reaction rate. The next time step is determined as a function of the propellant decomposition equations. Any equation involving the propellant decomposition may be used for this although some experimentation is required to find the most efficient equation. The fastest time step is then repeated and finally the last time step is a function of the propellant decomposition equations. The program is flexible so that the time steps can be altered during a run if desired to allow for special cases.

The technique used here is related to that adopted in reference 5 although the implementation is different. A variety of time steps are chosen so that all derivatives may contribute in varying degrees. For example 10 time steps of length $10\text{E}-17 \text{ sec}$ then 30 of length $10\text{E}-13 \text{ sec}$, followed by 10 at $10\text{E}-17 \text{ sec}$ and 3 at $10\text{E}-12 \text{ sec}$, 10 at $10\text{E}-17 \text{ sec}$ and 2 at $10\text{E}-11 \text{ sec}$. The sequence is then repeated. The time steps are assigned to each reaction as a function of the characteristic time for any component in the reaction. Therefore, in starting a run, it is necessary to run a few time steps with very short times to obtain an approximation of the amounts of various gaseous substances formed. The time steps are revised at frequent intervals usually every three times the number of steps in each cycle. For example, in the above case, it would be every 195 time steps.

Finally it was found that atom conservation becomes difficult when using a PC. This was overcome by performing a count of atoms at the end of each time step and adjusting the number of free carbon, hydrogen, oxygen, and nitrogen atoms to conserve atoms. These were chosen since they are very reactive and quickly adjust in the following time step. The proposed scheme appears to work well for propellants due to the relative simplicity of the reactions involved and the limited number of different species involved.

RESULTS

The initial tests were undertaken on a mixture of one mole of H_2 and half mole of O_2 . The program was tested against results obtained from the chemical equilibrium code MCVEC. The results were obtained at 1000 K/6 atm and at the adiabatic flame temperature of 3600 K/20 atm. The results are shown in table 1.

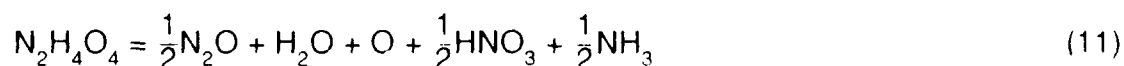
Table 1. Comparison of minimum free energy and reaction kinetics for $H_2 + \frac{1}{2}O_2$ at 1000 K and 3600 K

Species	Mole fractions			
	1000 K		3600K	
	MCVEC code	Kinetic code	MCVEC code	Kinetic code
H_2O	1.0000	0.9907	0.68	0.73
H_2	<10E-5	0.0015	0.08	0.16
H	<10E-5	0.002	0.05	0.02
OH	<10E-5	0.004	0.20	0.002
O	<10E-5	0.0004	<10E-5	0.0001
O_2	<10E-5	0.0014	<10E-5	0.007

At 1000 K, the kinetic and equilibrium codes are in good agreement (table 1), but a noticeable difference between the two codes is observed at the higher temperature where the equilibrium code yields less H_2O and more OH than the kinetic code. Since

published reaction rates for the water-OH reactions vary over a wide range, a mean value was chosen for the present test. The time variation of the species at 3600 K is shown in figure 1.

The program was then tested using the experimental results (ref 6) for HAN. The HAN was heated from 300 K to 650 K in 10 seconds. The kinetic code allows for this change of temperature as a linear variation. The implementation of the code requires the use of various simple reactions as well as an initial breakdown scheme for the HAN. The initial breakdown equation used was



The final equilibrium results were obtained using the MCVEC code for ideal gases. The proposed reaction kinetic scheme was used to model the heating, and the results are shown in figure 2. A comparison of the final states using the three methods is shown in table 2. The experimental results are in volume fractions, and the calculated ones are mole fractions. In addition, the experimental values do not include species which are IR inactive nor was the water volume measured. Therefore, the experimental values only show the relative proportions of the different species.

Table 2. Comparison of experimental, equilibrium, and kinetic results for HAN heated to 650 K and 1 atm

Species	Experimental volume fraction	Mole fractions	
		MCVEC code	Reaction kinetic
HNO ₃	0.76	<10E-5	0.135
NO ₂	0.2	<10E-5	<10E-02
N ₂ O	0.02	<10E-05	<10E-02
N ₂	-----	0.250	0.2236
H ₂ O	-----	0.500	0.5106
O ₂	-----	0.250	0.125
NO	-----	<10E-05	0.0011

The experimental results shown in table 2 considerable HNO_3 compared to the NO_2 formed. This is probably due to the way the HAN decomposed which strongly suggests that the equilibrium calculations are very long-time results; much longer times than are of interest in gun calculations. The amount of HNO_3 shown by the kinetic code is not necessarily incorrect since the amount of HNO_3 from the experimental results can only be compared to the nitrogen oxides formed. As these were not produced by the kinetic code, a comparison cannot be made. It suggests that considerable work is needed to determine correct reaction rates for HNO_3 because only limited data are available. The amount of water calculated by both codes is approximately the same. The kinetic code predicts more N_2 and less NO_2 than the equilibrium code. It appears that measurements of the water formed would be a useful measure to judge the accuracy of the calculations. The decomposition products of HAN when heated from 300 K to 1600 K and 15 atm were calculated and measured by all three methods. The results are shown in table 3.

Table 3. Comparison of experimental, equilibrium, and reaction kinetic results for HAN heated to 1600 K and 15 atm

Species	Experimental volume fraction	Mole fractions	
		MCVEC code	Reaction kinetic
HNO_3	0.2	<10E-05	0.114
NO_2	0.28	<10E-05	<0.01
N_2O	0.5	<10E-05	<0.01
N_2	-----	0.249	0.22
H_2O	-----	0.499	0.525
O_2	-----	0.249	0.05
NO	-----	0.0015	0.0107

Again the equilibrium calculations failed to show the formation of HNO_3 while the kinetic code produced a significant amount. The water produced in both the calculations was approximately the same. Problems with the formation of nitrogen oxides were apparent in the kinetic code.

CONCLUSIONS

The kinetic code appears to clearly show that it agrees well with the equilibrium code for long run times. There remains some doubt about the formation of HNO_3 and nitrogen oxides when compared to experimental results. This suggests that the equilibrium codes are not always suitable for gun calculations because it may require times much longer than milliseconds for the gun reactions to reach equilibrium.

RECOMMENDATIONS

Further development of this code will involve studies of the wet HAN, dry TEAN, wet TEAN, dry HAN/TEAN, and LP1845/1846. There still remains additional research to be undertaken on optimizing the code and allowing for certain reaction paths to be blocked due to three body effects. The inclusion of transport properties will be necessary before the hydrodynamic model can be developed.

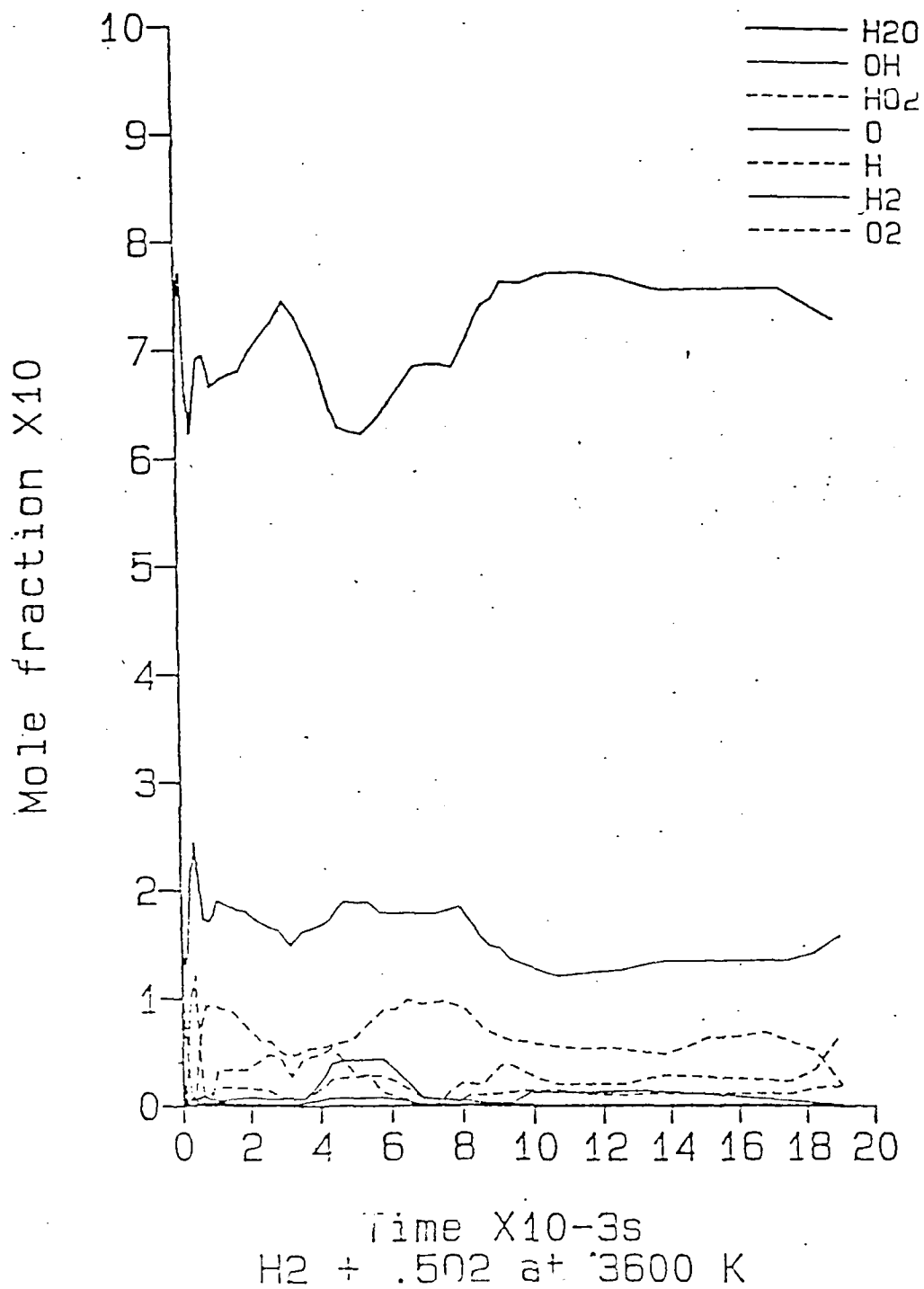


Figure 1. Variation of species with time for $\text{H}_2 + \frac{1}{2}\text{O}_2$ at 3600 K

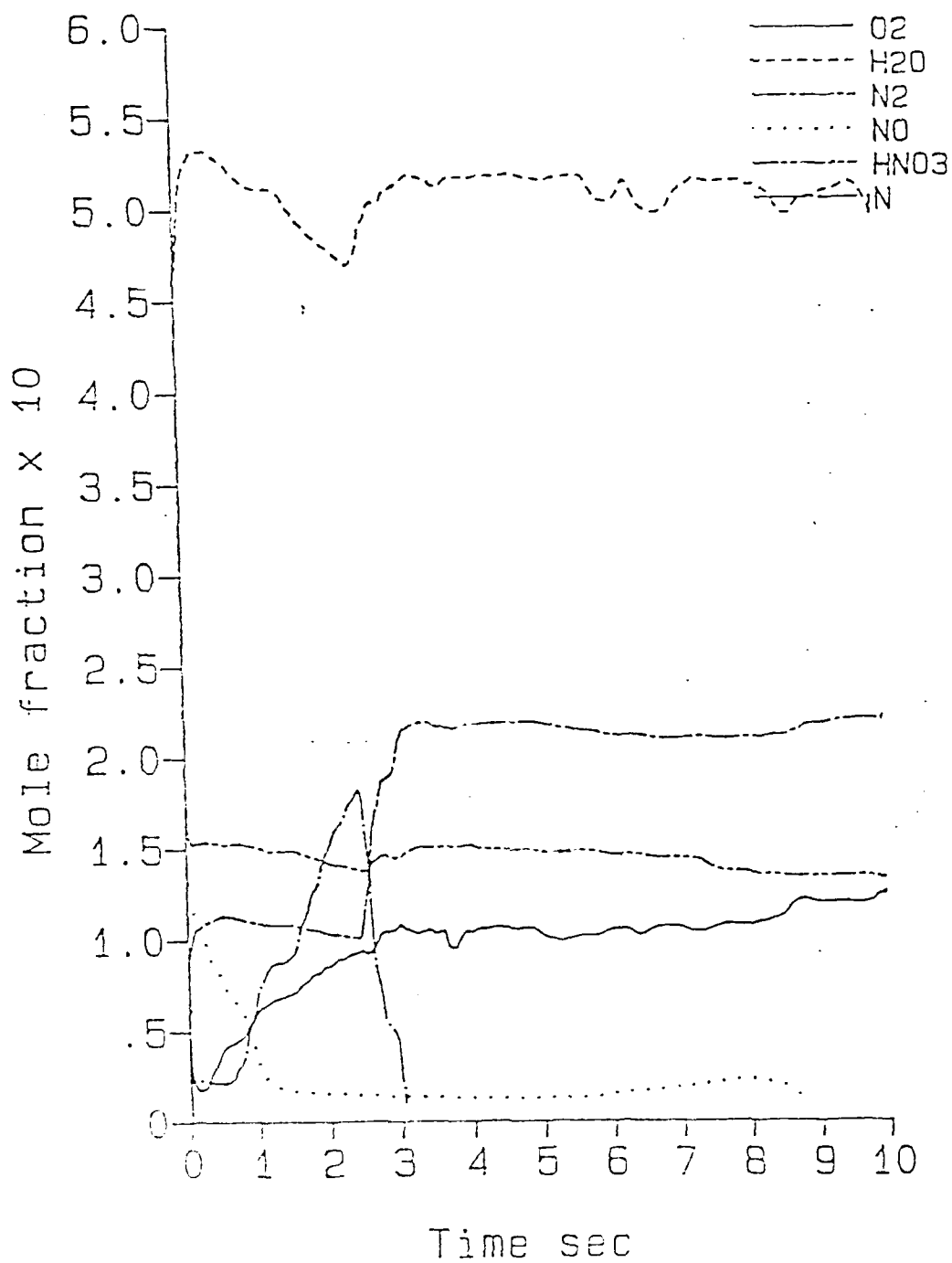


Figure 2. Variation of species with time for HAN heated to 1600 K and 12 atm

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